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Mono- and binuclear complexes of low-valent zirconium

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Chapter I

I.1 Introduction

The rich chemistry exhibited by group IVB transition metals is central to their role in organometallic chemistry. Many important reactions, particularly those involving Ti(IV) and Zr(IV) complexes, have not only attracted much academic attention but have also demonstrated their potential use in industrial applications. For example, olefin cationic polymerization¹, insertion of CO,² hydrozirconation³ and metal-promoted organic syntheses³, are of current interest in organometallic chemistry.

It is, however, somewhat surprising that attention in this field has been focused exclusively on complexes with cyclopentadienyl ligands and the reactions and reactivity of IVB transition metals using other ligands has been largely ignored⁴. Only a few complexes have been obtained using macrocyclic⁵ or Shiff base ligands⁶ and only a few phosphine⁷, arene⁸ and metal carbonyl derivatives⁹ have been reported. Even the understanding of the cluster chemistry of these metals, especially of Zr and Hf, is at present quite poor¹⁰.

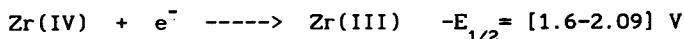
A unique aspect in the chemistry of zirconium and hafnium is that the formal oxidation state of (+IV) by far dominates both the coordination and organometallic chemistry. Although the chemistry of the di-valent Zr and Hf bis-cyclopentadienyl derivatives has been quite extensively studied and general reviews covering the synthesis and reactivity aspects have been published¹¹, the chemistry of the oxidation state (+II) remains almost unknown with the exception of the metallocenic species¹². The chemistry of zirconium and hafnium in the (0) and (-II) state is becoming documented¹³, but Zr(III) remains

rather elusive. The literature background is sparse and intriguing¹⁴. This lacuna in the chemical literature exists in spite of the potentially rich chemistry which can be expected by analogy with the well-known Ti(III)¹⁵. Two possible reasons can be postulated for this paucity of literature for Zr(II-III) and Hf(II-III):

1-Lack of appropriate ligands able to stabilize the lower oxidation states without perturbing at the same time the reactivity of the metal center. For example the involvement of the Cp rings in the reduction of IVB transition metal complexes is well-known¹⁶. Attempts to generate the metallocenic species Cp_2M in absence of stabilizing ligands result in the formation of very reactive derivatives able to perform oxidative addition to the C-H bond of the Cp ring.

2-The absence of selective reducing agents to achieve the oxidation state +II and +III.

For example, the low reduction potential¹⁷ for the following process:



precludes the possibility of using the mild reducing reagents (e.g. Zn or Al) commonly used in the preparation of Ti(III) derivatives¹⁸. Stronger reducing agents like Na, Li, Mg as metals, amalgams or naphthalene complexes are required. There is however, no guarantee that further reduction to zero-valent species or even negative oxidation states will not take place.¹⁹

The methods used for the preparation of Zr(II-III) species can be summarized in four different synthetic pathways¹⁴:

- reduction of Zr(IV) complexes
- comproportionation reaction between complexes having the metal in different oxidation states
- selective oxidation of low-valent derivatives
- ligand-substitution reactions on Zr(II-III) inorganic complexes

I.2 Scope of this thesis

This thesis is a study on the synthesis and reactivity of low-valent zirconium. The investigation can be divided in two parts: the first describes the chemistry of mono-cyclopentadienyl Zr(II) complexes (Chapter II, III and IV), and the second describes some synthetic pathways successfully used for the preparation of metallocenic and related type Zr(III) complexes. (Chapter V and VI).

When we started the present investigation, the chemistry of Zr(II) was limited exclusively to the bis-cyclopentadienyl systems. This was as rule with no exceptions. We argued that half sandwich Zr(II) compounds (e.g. mono-cyclopentadienyl) might provide a possible, alternative class of new compounds characterized by higher reactivity of the metal center. The preparation of a suitable starting material to develop this chemistry was achieved by reduction of $\text{CpZrCl}_3(\text{THF})_2$ with Na in THF in the presence of 2 eq dmpe. The reaction allowed the preparation of the first divalent zirconium half-sandwich complex $\text{CpZrCl}(\text{dmpe})_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane). The synthesis and the electrochemistry are discussed in chapter II.

This complex is indeed characterized by its high reactivity. The coordinatively and electronically unsaturated intermediate $\text{CpZrCl}(\text{dmpe})$, which is obtained in situ from $\text{CpZrCl}(\text{dmpe})_2$ via easy dissociation of one of the two chelating phosphines, displayed a versatile reactivity towards several organic substrates including CO, olefins, di-olefins and acetylenes.

The synthesis and characterization of the first example of a low-valent zirconium alkyl complex, $\text{CpZrMe}(\text{dmpe})_2$, are discussed in chapter III. In contrast to the behaviour of the well-known high-valent congeners, the complex showed an unexpected inability to insert olefin into the Zr-C bond. Stoichiometric reductive coupling took place with ethylene, to form a new class of butadiene complexes: $\text{CpZrR}(\eta^4\text{-butadiene})(\text{dmpe})$. The synthesis, reactivity and catalytic features of these complexes are discussed in chapter III.

Reductive coupling of light alkynes led to the formation of metallo-cyclopentadienes. An unusual hydrogen-transfer reaction between two molecules of alkyne was observed in the presence of bulky substituents. A possible rationalization of these features and of the catalytic alkyne cyclotrimerization is described in chapter IV.

The high tendency to reduce unsaturated organic substrates, with consequent increase of the oxidation state of the metal [from (II) to (IV)] emerged as a main characteristic of the reactivity pattern of Zr(II).

We argued that the reactivity of Zr(III), probably characterized by the radical behaviour of the d^1 metal centre, might be interesting although less predictable. However, very little was known about this chemistry when we started this investigation. $[\text{ZrCl}_3(\text{PR}_3)_2]_2$ was the only thoroughly characterized Zr(III) complex. The mono-cyclopentadienyl Zr(III) systems are unknown, and only the preparation of bis-cyclopentadienyl zirconium(III) mono-halides had been reported in the literature. The stability properties and colors assigned to these species were contradictory, making their existence questionable at the least.

Our attempts to obtain metallocene Zr(III) complexes via reduction of the corresponding Zr(IV) derivatives using alkali-metals failed, due to lack of selectivity of the reducing agents. The successful preparation of the series $[\text{Cp}_2\text{ZrX}]_2$ [$\text{X} = \text{Cl}, \text{Br}, \text{I}$] was obtained via photolysis of $\text{Cp}_2\text{Zr}(\text{R})\text{X}$ [$\text{R} = \text{}^i\text{Bu}$]. The synthesis and stability properties of these complexes are described in chapter V.

Unfortunately, the high tendency of $\text{Cp}_2\text{Zr}^{\text{III}}\text{X}$ complexes to disproportionate to $\text{Cp}_2\text{Zr}^{\text{IV}}\text{X}_2$ and " $\text{Cp}_2\text{Zr}^{\text{II}}$ " hampered their use for an extensive investigation of their reactivity. In principle it is possible to prevent the undesirable disproportionation reaction by means of binucleating ligands. A ligand in which two cyclopentadienyl rings are linked together by a single C-C bond ($\eta^5:\eta^5$ -fulvalene), might work as a suitable system to verify this idea and to develop the chemistry of trivalent zirconium.

Binuclear, fulvalene containing Zr(III) and Zr(IV) complexes were

prepared via selective oxidation of $[(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{CpZrPMe}_3]_2$ with several oxidizing agents: R_3PX_2 , PhSSPh and Me_2PPMe_2 leading to the coupling of the two $(\eta^1:\eta^5\text{-C}_5\text{H}_4)$ rings and the formation of the $\eta^5:\eta^5$ -fulvalene moiety. The reaction with an organic azide led to the oxidation of the two metal centers to form a bridging imido-complex. The synthesis and reactivity of these species are described in chapter VI.

I.3 X-Ray diffraction

Several complexes described in this thesis have been characterized by X-ray diffraction. A full report of the experimental details is available in the publications in which this chemistry has been described. In this thesis the appendix gives a comprehensive list of all structural parameters of the complexes and the name of the crystallographer who solved the structure.

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